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Analysis of Complex Alloys

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# THE ANALYSIS OF COMPLEX ALLOYS

With Special Reference to the Determination of  
Tin, Arsenic and Antimony

BY

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THESIS FOR THE DEGREE OF BACHELOR OF SCIENCE

IN CHEMISTRY

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An alloy may be designated as a mixture of two or more metals formed by fusion. The majority of metals can be fused together in any proportion desired and by introducing certain metals and varying the percent of others different properties can be given these different alloys.

Alloys were known as far back as the time of Pliny and Romulus but alloys in those times were very crude as compared with the mixtures of to-day. For instance the alloy of copper and tin which is generally called bronze contains now besides these two metals lead and zinc. It must be remembered that zinc in a metallic state was not known until later years, so it excuses them from its use. Mercury however was known to the ancients and was used by them in the form of amalgams as can be seen by the statue of Marcus Aurelius which now stands in Rome and which is covered with a coating of gold amalgam.

Thus we see that while the old Greeks and Romans understood the making of bronze and amalgams, their only mixtures of metals consisted of the alloys of copper, tin, zinc, silver, and gold. To prepare other alloys a greater knowledge of chemistry was required than they possessed at that time, but as this science developed and the mixing of metals became better known, new difficulties presented themselves. The alloying of metals has not by any means reached its height of perfection but still at the present time we know what properties certain metals have, what properties different metals give by adding them to certain other metals or mixtures of metals.





Some increase specific gravity, others ductility, others hardness, brittleness, etc. until at the present time most alloys contain four or five but generally seven or eight different metals. The problem then is what is the percent of each metal in the alloy. from the fact that an alloy containing five percent of copper would vary greatly in properties from the same alloy containing twenty-five percent, we must have a method by which we can quickly and accurately determine the composition of said alloys.

Consider for instance the bronzes, gun metals, bell metals, amalgams, babbitts, German silvers, white metals, type metals, solders, etc., etc. We can easily see what a large field we are entering and the necessity of an accurate method for the determination of their constituents. Another important thing is the replacement of cheaper metals in an alloy for the more expensive. Tin for instance is lowered in percentage and copper and lead substituted giving the same properties as the tin with the exception of hardness. This is furnished by the addition of antimony.

As far as the determination of tin, arsenic, and antimony in alloys is concerned, a great many different methods have been proposed. Most of them however depend upon the separation of the sulphides of the tin, arsenic and antimony from the other sulphides of the second group by the means of yellow ammonium sulphide. All methods involving the use of this reagent are tedious as well as inaccurate from the fact\$ that the yellow ammonium sulphide must be in contact with the sulphides for hours before the tin, arsenic and

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antimony sulphides will be entirely dissolved. Separation of quantities of sulphur is also very annoying. The yellow sulphide also dissolves the sulphides of copper and bismuth so here again we meet another difficulty. In fact all methods involving the use of this reagent besides being tedious are very unreliable and inaccurate. There are numerous other processes some of the principal of which are Drown's, Bunsen's, Garnot's, Clarke's, Kassner's, Warren's, Weller's and others.

Drown's method depends upon the volatilization of the chlorides of tin, arsenic, and antimony and the absorption of the same in potassium bromide; arsenic is distilled from this solution and the tin and antimony separated according to Garnot's method.

Garnot's method treats a neutral hydrochloric acid solution of tin and antimony with oxalic acid in excess. This excess of oxalic acid prevents the precipitating of the tin, when by adding sodium thiosulphate the sulphide of antimony comes down. If the oxalic acid is not in excess the tin will precipitate; in fact sometimes, the tin precipitates in small amounts anyway and here is where the difficulty lies. The precipitation of the antimony is very complete but the tin occasionally mixed in and hence results vary at times.

Bunsen's method precipitates the salts of arsenic and antimony as sulphides with  $H_2S$ . These sulphides are then treated with KOH solution generally five percent. This easily dissolves these sulphides and puts them into solution as arsenates and antimonates. This solution is then put into a suitable flask and the arsenic is





volatilized by means of chlorine gas, thus affordind a separation of the two. The main difficulty in the process is the volatilization part, because at last it is impossible to collect the entire contents and also to cause complete volatilization. The use of 5% KOH is alright because there is no tin present, but if it were, the strength would have to be lowered.

This method is open to criticism because most alloys contain tin and this method does not deal with it, and besides that if antimony and arsenic alone are to be determined, also any method depending on the volitalization of the arsenic is almost certain of rejection in technical work.

Kassner treats the sulphide of tin, arsenic, and antimony with  $\text{Na}_2\text{O}_2$ . This causes the sulphide of arsenic and antimony to go into solution but the tin partially precipitates. Upon acidifying tin oxide comes down. By continual boiling and addition of alcohol pyroantimonic acid separates out. This method is worthless because in no case could I obtain complete precipitation of pyroantimonic acid.

Warren's method has to deal with the separation of tin from antimony. Solutions of the metal are treated with  $\text{H}_2\text{S}$  when the sulphides are precipitated. A solution of NaOH is then added to put the tin and antimony sulphides into solution thus enabling a separation of Bi, Cu, and other second group metals. To the filtrate HCl was added, the sulphide filtered off dissolved in aqua regia.

$\text{K}_4\text{FeC}_6$  was then added to the solution and the tin was precipitated as stannic ferrocyanide. Antimonic ferrocyanide is unknown. The





main difficulty in this method is with the strength of the NaOH. The strength was not given, but if it were stronger than one percent, or added in larger quantities at a time the Sn would precipitate. Unless these conditions are regulated the method is not reliable.

If solutions of sulphides of tin, arsenic, and antimony in sodium sulphide be boiled with CuO they will be converted into the stannate, antimoniate, and arsenate respectively. To the filtrate alcohol is added and if antimony be present it will be precipitated as pyroantimonic acid. In the filtrate the alcohol is boiled off and  $\text{NH}_4\text{Cl}$  added in excess. A milk-white precipitate indicates the presence of tin.  $\text{H}_2\text{S}$  is passed thus dissolving the precipitate. The solution is then made alkaline and the arsenic precipitated with magnesium mixture. The tin in the filtrate is precipitated by means of  $\text{HCl}$ . This method is probably alright for arsenic and possibly tin, but my experience has been that complete precipitation of antimony by this method is impossible.

Dr. A. Weller's method deals with the separation of antimony from tin. Metallic antimony was dissolved in  $\text{HCl}$  and the solution oxidized with  $\text{HClO}_3 + \text{HCl}$  and heated to expel excess of  $\text{Cl}$ . The solution of  $\text{SbCl}_5$  was then put into the Bunsen chlorine distillation apparatus and mixed with  $\text{KI}$  not in excess. The liberated  $\text{I}$  was distilled with  $\text{KI}$ . When cold this was titrated with  $\text{H}_2\text{SO}_3$ . This method is based upon the fact that stannic acid and  $\text{SnCl}_4$  in acid solution do not decompose  $\text{KI}$ . I see no reason why this method should not be fairly accurate if the distillation can be carried on successfully, but as yet all distillation methods are not of much value.



H. Causse has developed a volumetric method for antimony which is based upon the fact that when antimonious acid either free or combined comes into the presence of iodic acid, the latter is destroyed and the antimonious acid passes to antimonic acid while I is liberated.  $5\text{Sb}_2\text{O}_3 + 2\text{IO}_3 = 5\text{Sb}_2\text{O}_5 + 2\text{I}$ .

Thus we have given a fairly complete outline of the methods now in use. It has always been known that sulphide of tin, arsenic, and antimony were soluble in fixed alkali, but in the few methods where the dissolving power of the alkali was used no results could be obtained and in fact the conditions have never been studied. In the method which I will describe potassium hydroxide is the alkali which is used.

The first question is what is the solvent action of KOH in the sulphides of the second group and what is the proper strength for our alkaline solution. At first a 2% solution was tried. Precipitates of sulphides of all the metals of the second group were made and it was found that only the tin, arsenic, and antimony sulphides were soluble in this medium. Arsenic and antimony sulphides were very soluble and after the addition of the potassium hydroxide, the solution could be boiled without any change taking place in the solution.

Tin however acted differently; it was plainly seen that the stannous sulphide could not be used because it was hardly soluble in the medium. Stannic sulphide which was easily soluble in the hydroxide but on boiling the tin was precipitated as metastannic acid or tin hydroxide. I next tried different strengths of the





solutions of potassium hydroxide varying from 5% to 1/5%. As soon as a 1% solution of KOH was reached, this precipitation upon boiling ceased and in fact with the two percent solution, it only came down after continued boiling. I again tried the solubility of the 1% KOH upon the various sulphides with the same result. Mixtures of the sulphides were then tried only to verify the above statement.

From the fact that 2% KOH precipitates tin hydroxide from the solution while 1% KOH does not, it can plainly be seen that an excess of KOH is to be avoided. This was prevented in the following manner. Sulphides of tin, arsenic, and antimony were taken individually and 1% KOH added to each solution from a burette until they were all alkaline. This point was reached in each case before the sulphides were dissolved. The amount of KOH added in each case was noted and then more was added. When double the amount of alkali had been added, the precipitates were completely dissolved. These solutions stood boiling without any precipitate being formed because the alkali had been added slowly preventing an excess, and as yet an excess had not been added. More KOH was added to each and it was not until five times the amount necessary to produce alkalinity had been added did the tin start to precipitate. This being considered it was decided to use three times more the amount KOH than was required to make the solution alkaline. The amount of alkali to be used on this theory was then put to the test. ¶ To begin with the alloy to be analyzed is dissolved in con. HCl to which a small amount of  $\text{HNO}_3$  has been added. The best proportion that I found was 25cc con. HCl and 5cc Con.  $\text{HNO}_3$  using .2 gram of the alloy





to be analyzed. After numerous experiments with different amounts of the alloy to be taken, it was found that .2 of a gram was the best. Any larger amount gives too large an amount of precipitate to work with. The acid is added to the weighed sample of the alloy in a beaker and dissolved with the aid of heat. In case solution is not complete or crystals of salts are formed, it is best to add about 15-20cc more of the acid and continue the heating. When solution is complete, 10cc of  $H_2O_2$  are added and the solution boiled to get rid of the excess of peroxide. This peroxide is added to change any stannous salts which might be present to stannic. However it is necessary to boil off the excess of peroxide or else it will interfere slightly when  $H_2S$  is added. The solution is now taken and diluted six or seven times its volume and heated. While hot  $H_2S$  is passed through the solution for fifteen minutes to precipitate all metals of the second group. After precipitation is complete a little  $H_2O_2$  is added, say 5cc to aid filtration. A few cc of  $H_2S$  water are also added to throw back any copper which might have been dissolved. The solution is next filtered and washed. The filtrate is saved because it contains the Zn, Al, or whatever other metals might be present which have not been precipitated. The above filtration is done in a Hirsch funnel using asbestos. Now the asbestos and precipitate are washed back into the beaker and care must be taken to keep the amount of water small; the amount of water and ppt. should be about 50cc. Now to cold solution and precipitate 1% KOH is run in from a burette slowly until the solution reacts alkaline. The KOH must be added drop at a time and keeping the solution stir-



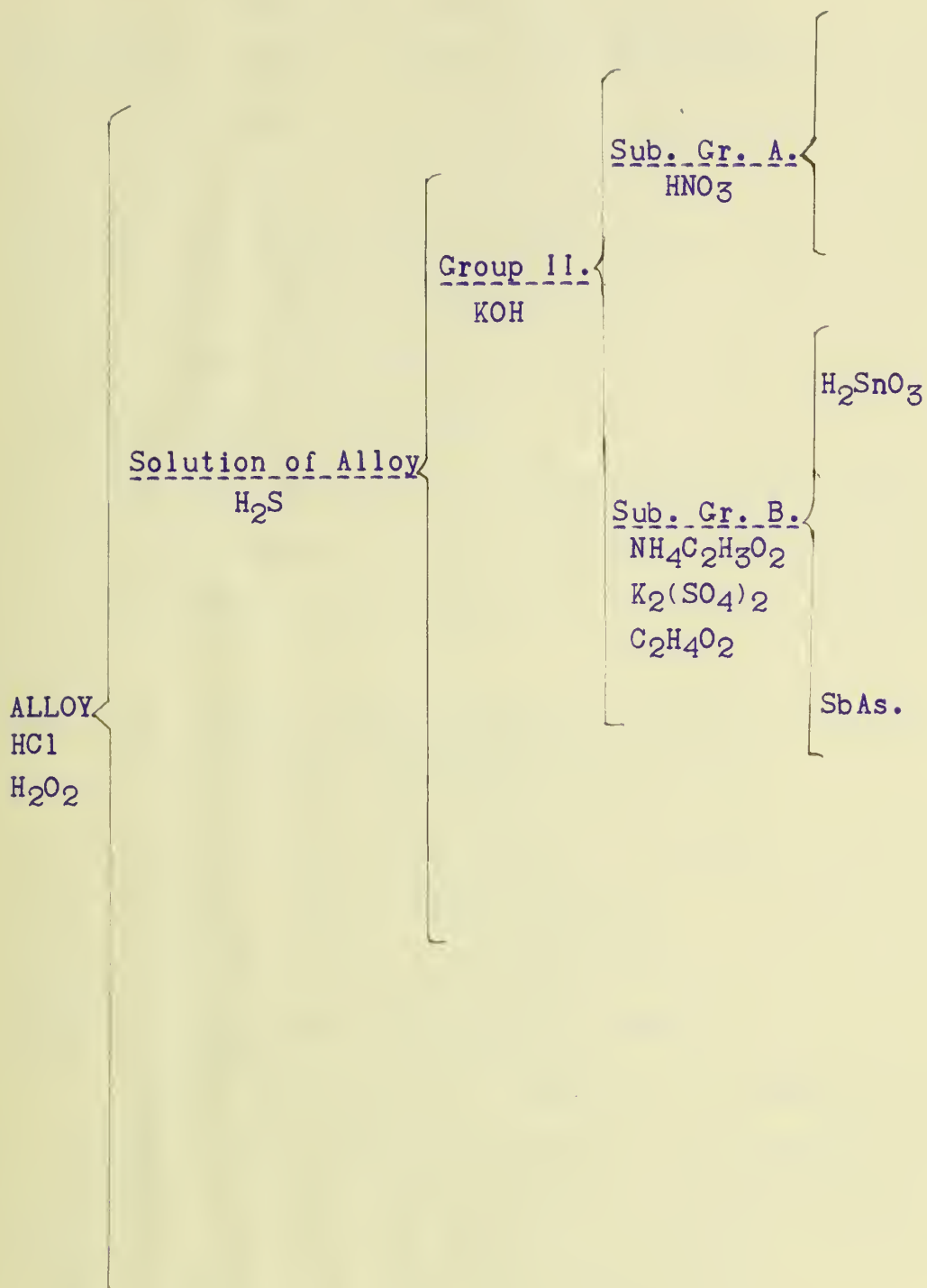
red during the addition. When the alkaline point is reached, the burette reading is noted and then three times more this amount is added as before. When the required amount has been added the solution is taken and heated and boiled for three or four minutes. This is then filtered on a filter paper, the precipitate washed thoroughly and we now have the tin, arsenic, and antimony in the filtrate in solution. The precipitate contains the copper, lead, cadmium, mercury, and bismuth.

I now took the filtrate, heated it to boiling, added 10cc of  $H_2O_2$  to make sure of oxidation, and boiled for three or four minutes. I next added 15cc of ammonium acetate to keep back the antimony. Then I added  $K_2SO_4$  about 10-15 grams and boiled. If no precipitate is formed, I added a few cc of acetic acid to bring the solution up to the neutral point. When the neutral point was reached the tin was precipitated completely as  $Sn(OH)_4$ . This can be filtered off and weighed as  $SnO_2$ .

Magnesium mixture is added to the filtrate and if any arsenic is present, it will precipitate and can be determined as magnesium ammonium arsenate. To the filtrate  $H_2S$  is added and the antimony precipitated as the sulphide  $Sb_2S_3$ . This is filtered on a hardened filter paper and the precipitate washed off the filter paper into a casserole where it is heated with fuming  $HNO_3$ . This changes the sulphide into an oxide. After evaporating to dryness and being sure that all sulphide is converted into oxide, it is filtered on a carefully prepared gooch and weighed as the oxide. Thus we have a detailed account of the method for the separation and determination of tin, arsenic, and antimony in an alloy.











# RESULTS OF LABORATORY WORK.

$\text{PbS} + 5\% \text{ KOH} + \text{heat} = \text{Trace of PbS dissolved.}$

$\text{PbS} + 2\% \text{ KOH} + \text{heat} = \text{'' '' '' ''}$

$\text{PbS} + 1\% \text{ KOH} + \text{heat} = \text{No trace of PbS.}$

$\text{PbS} + \text{KOH in excess} = \text{very slight trace.}$

$\text{PbS} + \text{Alcoholic KOH} = \text{no PbS dissolved.}$

$\text{PbS} + \text{KOH} + \text{KCO}_3 = \text{insoluble}$

$\text{PbS} + \text{KOH} + \text{NH}_4\text{SO}_4 = \text{insoluble.}$

$\text{CuS}$ ,  $\text{CdS}$ ,  $\text{HgS}$ ,  $\text{Bi}_2\text{S}_3$  all act with the  $\text{KOH}$  practically the same as the lead. The copper sulphate acts exactly the same while the  $\text{CdS}$ ,  $\text{HgS}$ , and  $\text{Bi}_2\text{S}_3$  all are insoluble in the dissolving potassium hydroxide.

$\text{CuS}$   $\text{KOH}$   $\text{NH SO}$  almost complete solution(a little  $\text{H}_2\text{S}$  water).

$\text{SnS}_2$   $5\% \text{ KOH}$   $\text{heat}$   $\text{Sn(OH)}_4$ as precipitate.

$\text{SnS}_2$   $2\% \text{ KOH}$   $\text{heat}$  precipitate of  $\text{Sn(OH)}_4$

$\text{SnS}_2$   $1\% \text{ KOH}$   $\text{heat}$  clear solution.

$\text{SnS}_2$   $1/2\% \text{ KOH}$   $\text{heat}$  clear solution.

$\text{SnS}_2$  alcoholic  $\text{KOH}$  gives same results.

In all cases the  $\text{KOH}$  must be added from a burette and must be added drop at a time so that the  $\text{KOH}$  will not be present in excess in contact with the precipitate, because whenever the  $\text{KOH}$  is in excess, the tendency is for the tin to precipitate.

$\text{SnS}_2$   $\text{KOH}$   $\text{H}_2\text{O}_2$  turbid solution which upon boiling precipitates the tin.

$\text{SnS}_2 + \text{KOH} + \text{KSO}_4 = \text{tin precipitated as Sn(OH)}_4.$

$\text{SnS}_2 + \text{KOH} + \text{KCO}_3 = \text{'' '' '' ''}$

$\text{SnS}_2 + \text{KOH} + \text{NH}_4\text{SO}_4 = \text{'' '' '' ''}$



These last three reactions are true in all cases. In the case of the oxidation with  $H_2O_2$ , the tin will not be precipitated unless the KOH has a strength of 2% or more and then complete precipitation cannot be depended upon.

$K_2SnO_3 + KSO_3$  = complete precipitation of Sn } Acetic acid aids  
 $K_2SnO_3 + NH_4SO_4$  = ' ' ' ' } complete precipit'n.

$As_2S_3 + 5\% KOH$  = clear solution.

$As_2S_3 + 2\% KOH$  = ' ' ' '

$As_2S_3 + 1\% KOH$  = ' ' ' '

$As_2S_3 + 1/2\% KOH$  = ' ' ' '

$As_2S_3 + KOH + KSO_4$  = ' ' ' '

Precipitated easily however with magnesium mixture.

$Sb_2S_3 + 5\% KOH$  = solution clear.

$Sb_2S_3 + 2\% KOH$  = ' ' ' '

$Sb_2S_3 + 1\% KOH$  = ' ' ' ' clear after at least three extractions have been made. The antimony sulphide is easily soluble in 2% KOH or stronger, but if the KOH is weaker, two extractions should always be made. The oxide never precipitates upon boiling and the only precaution is complete solution.

$K_2Sb_2O_5 + KOH + KSO_3$  = upon boiling gives precipitation.

$K_2Sb_2O_5 + KOH + KSO_4 + NH_4C_2H_3O_2$  = clear solution upon long boiling. The acetate is necessary in all cases wherever antimony is present because it is entirely soluble in this medium. If it were not added the oxidizing effect of the  $KSO_4$  which is used to precipitate the tin would precipitate the antimony as well. Only a small amount is needed, say 10cc.





It is necessary to have the tin in the stannic form before addition of the KOH because all experiments with stannous sulphides proved to be failures. The  $\text{SnS}$  will not dissolve in KOH. Upon the addition of  $\text{H}_2\text{O}_2$  the sulphide is oxidized and after several treatments goes into solution. This cannot be done in practice however because the point of complete oxidation and solution cannot be determined.

In treating the sulphides of copper and lead with the  $\text{KSO}_4$  and  $\text{NH}_4\text{SO}_4$  some peculiar reaction took place. Especially in the case of the persulphate of ammonia. The persulphate dissolves all the copper sulphide and leaves the tin and lead precipitated. These could easily be separated and it looks like this could be developed into a method and much time was spent upon it. The ammonium persulphate in the presence of ammonia has a great oxidizing effect and is strong enough to precipitate all the tin as hydroxide. It has no effect in the lead while it dissolves the copper. The main difficulty is that the copper sulphate cannot be separated completely from the precipitate. It seems as though the precipitate cannot be washed clean. I tried the addition of  $\text{H}_2\text{O}_2$  but it did not change matters.

I next tried the above with  $\text{KSO}_4$  instead of  $\text{NH}_4\text{SO}_4$  with the result that all the tin was precipitated and the lead still remained unchanged. The copper however in this case was about half dissolved and existed in filtrate and precipitate. I could find no way to make complete separation of Cu by these methods and hence the work was discontinued and the KOH method of solution was perfected.





Returning to the KOH method, the difficulties were overcome and the method seems to be fairly accurate. The difficulties were strength and amount of KOH to be used and  $\text{KSO}_4$  and acetic acid precipitate, all the Sn without any Sb or As. After these had been straightened out the quantitative work was commenced. The Sn determination seems to be all right but the Sb varies too much which I think is due to volatilization. In the treatment of the sulphide with fuming  $\text{HNO}_3$  to expel the sulphur, I think the Sb is volatile to some extent but if neat precaution and care are taken the error should be kept very small.



BABBITT NO. 5.

New Method.

4.41% tin

7.4% antimony

4.72% tin

7.21% antimony

4.26% antimony.

BABBITT NO. 4.

New Method.

1.96% tin

5.26% antimony

1.84% tin

4.31% antimony

1.91% tin

7.26% antimony.

BABBITT NO. 3.

3.25% tin

2.41% antimony

3.31% tin

3.16% antimony.

BABBITT NO. 2.

7.00% tin

18.2% antimony

7.60% tin

17.3% antimony.

8.51% tin

7.61% tin.

BABBITT NO. 1.

8.1% tin

11.41% antimony

8.4% tin

11.62% antimony.





QUANTITATIVE WORK.

Tried method on a brass sample containing 7.1% tin.

New Method

	7.57% tin
	7.14% tin
% Sn by other methods	7.18% tin
7.1% tin.	7.32% tin
	8.21% tin
	7.26% tin

The principal reason for these variations were due to manipulation of the method and variations in conditions. After all conditions had been settled and I had become thoroughly familiar with the method I ran two duplicates at 7.21% and 7.36% Sn.

BABBITT NO. 7.

New Method.

1.427% tin	2.8% antimony
1.343% tin	4.2% antimony
1.550% tin	4.8% antimony.
.805% tin	
1.415% tin	

BABBITT NO. 6.

New Method.

6.31% tin	8.4% antimony
6.34% tin	6.1% antimony
6.96% tin.	5.32% antimony.





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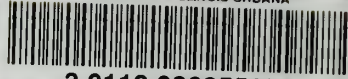








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